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Calculated orientation dependence of surface segregations in Pt₅₀Ni₅₀

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We present local-density calculations of surface segregation profiles in a random Pt₅₀Ni₅₀ alloy. We find that the concentration profiles of the three low-index surfaces oscillate and that the two most closely packed surfaces, i.e., (111) and (100), are enriched by Pt while Ni is found to segregate to the surface of the (110) face. These results may be explained in terms of a competition between the tendency of Pt to segregate towards the two first surface layers at the (110) face and the tendency to form a structure of alternating Pt and Ni layers.

The Pt-Ni system has attracted considerable interest owing to the most unusual orientation-dependent surface segregation profiles of its three low-index surfaces. As a result of recent experimental investigations it has been established that the two most closely packed surfaces (111) and (100) exhibit an oscillatory concentration profile with a Pt enriched surface layer.¹⁻⁵ Similarly, the more open (110) face is found to exhibit an oscillatory concentration profile, but in this case the surface layer is enriched by Ni,⁵⁻⁷ and hence, the segregation is reversed when going from the (111) or (100) faces to the (110) face. This reversal cannot be explained by phenomenological arguments in terms of the difference in surface energy or atomic size of the species and has therefore prompted a number of empirical and semiempirical calculations.⁸⁻¹⁴ To a varying degree of accuracy these calculations reproduce the experimental segregation profiles of the (111) and (100) faces but are at variance with each other and with experiments as concerns the profile of the (110) face. The situation may be summarized if we consider the 50% alloy. At this concentration, Lundberg⁸ who used the embedded atom method (EAM) found Ni segregation at the (110) face while Stadler *et al.*¹⁴ in a more recent EAM calculation found Pt segregation. Legrand *et al.*¹⁰ used a semiempirical tight-binding Ising model and also found Pt segregation for the equiatomic alloy. On the other hand, at lower Pt concentration both Legrand *et al.*¹⁰ and Stadler *et al.*¹⁴ found Ni segregation in agreement with the experimental results for the alloy with 10% of Pt in the bulk.

In the present work, we have determined the equilibrium concentration profiles of the three low-index surfaces of a random Pt-Ni alloy at a bulk concentration of 50% from first principles. To do so, we used a technique based on a combination of total energy calculations within the framework of density functional theory in the local density approximation (LDA) and statistical mechanics free energy calculations in the mean-field approximation. The electronic structure and

the total energy of the surfaces were calculated by means of the linear muffin-tin orbitals (LMTO) method in conjunction with the coherent potential approximation (CPA) and a Green's function technique.¹⁵⁻²³ The complete procedure has been described by Ruban *et al.*^{24,25} who used it to calculate segregation profiles in CuNi. In the present application the surface region was treated self-consistently and consisted of six layers of atomic spheres and two layers of vacuum spheres. The core electrons were included in all the self-consistent calculations and for exchange and correlation we used the Perdew-Zunger interpolation²⁶ of the many-body calculations of Ceperley and Alder.²⁷ The equilibrium lattice parameter of the alloy obtained in the bulk LMTO-CPA-LDA calculations is 3.777 Å in good agreement with the experimental value of 3.749 Å.²⁸

To evaluate the total energy for a general segregation profile we use the Connolly-Williams method according to which the total energy of the alloy system is represented by a phenomenological expansion over the cluster functions in terms of concentration-independent interatomic interactions. For a completely disordered alloy with a surface such an expansion over layer number Λ may be written in the form

$$E = E_0 + \sum_{\Lambda=1}^{\infty} [(V_{\Lambda}^{(1)} - V_{\text{bulk}}^{(1)})\sigma_{\Lambda} + V_{\Lambda}^{(2)}\sigma_{\Lambda}^2 + V_{\Lambda+}^{(2)}\sigma_{\Lambda}\sigma_{\Lambda+1} + V_{\Lambda++}^{(2)}\sigma_{\Lambda}\sigma_{\Lambda+2} + \dots], \quad (1)$$

where E_0 is a reference energy, $V_{\Lambda}^{(1)}$ the one-site interactions, $V_{\text{bulk}}^{(1)}$ the corresponding bulk interactions, $V_{\Lambda}^{(2)}$ the two-site interactions in a layer, and $V_{\Lambda+}^{(2)}$ and $V_{\Lambda++}^{(2)}$ the two-site interactions between layers. Furthermore, σ_{Λ} denotes the average value of the spin variable $\sigma_{\Lambda p}$ which takes on the values $+1$ or -1 depending on the type of atom occupying site p in the

layer Λ . It is related to the layer Ni concentration c_Λ , i.e., $\sigma_\Lambda = 2c_\Lambda - 1$, and varies between -1 and 1 .

In spite of the phenomenological character of the Connolly-Williams expansion and the truncation which must take place to render a finite number of interatomic interactions, it turns out that the accuracy of (1) is well controlled. In the extraction we found that the bulk pair interactions for the second, third, and fourth nearest neighbors were one order of magnitude smaller than those of the nearest neighbors and also smaller than triangle and tetrahedron interactions indicating that the cluster expansion of the total energy is well converged. Moreover, we checked the accuracy of our parameters by calculating the total energies for a few concentration profiles not included in the extraction of the interatomic interactions. We found in all cases that the results of (1) agreed with the direct LMTO-CPA calculations to within the accuracy of the first-principles calculations (about 0.1 mRy).

As a result of the convergence properties of (1) we carried out a series of total energy calculations with prescribed concentration profiles where the concentration of the fifth and sixth layers were fixed at 50% providing a smooth fit to the bulk region. In total we treated 32 configurations for the (111) face and 21 configurations for each of the (100) and (110) faces. Based on these calculations we extracted the Connolly-Williams interactions^{29,24} up to tetrahedra of nearest neighbors by inversion of (1). Finally, we calculated the equilibrium concentration profiles within the mean-field approximation for the configurational entropy neglecting lattice relaxations and any other contributions, e.g., thermal vibrations, to the free energy of the alloy.

An alternative approach for calculating interatomic interactions is provided by the direct configurational averaging which is used in the generalized perturbation method (GPM) and which has been applied to the segregation problem by a number of authors.^{30,31} However, by definition the GPM only takes into account changes in the one-electron contribution to the total energy and does not account for the direct electrostatic interaction between atoms caused by charge-transfer effects. In particular, it is concluded by Singh *et al.*³² in a study of the phase stability of bulk Ni-Pt alloys, that the use of the GPM with only band energy contributions may be unreliable. In the present case it is therefore clearly preferable to apply the Connolly-Williams scheme in conjunction with total energy calculations which include one-electron contributions as well as charge-transfer effects in the system.

In Fig. 1 we present the calculated surface profiles for three low-index surfaces of $\text{Pt}_{50}\text{Ni}_{50}$. The results show in complete agreement with the experimental data oscillatory surface-concentration profiles for all three faces and a segregation reversal at the (110) face. Since the calculations include no adjustable parameters the quantitative agreement with the experimental profiles is a clear indication of the applicability of the Connolly-Williams technique in surface segregation studies.

The surface segregation reversal at the (110) face is an exception to phenomenological criteria according to which one would expect the element of lowest surface energy and largest atomic size to segregate to the surface. As may be seen from Table I where we summarize the calculated surface energies for pure Pt and Ni, Pt always has the lower surface

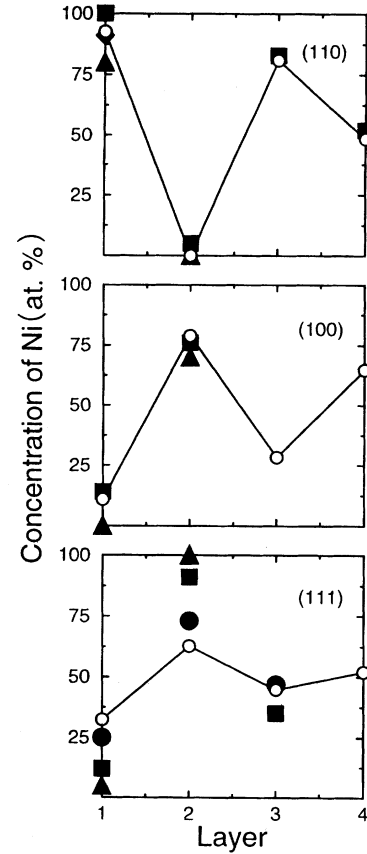


FIG. 1. Comparison of calculated and experimental segregation profiles for the three low-index faces of disordered $\text{Pt}_{50}\text{Ni}_{50}$. Full line: present results at 1000 K. Triangles: incidence-dependent excitation for Auger spectroscopy, Ref. 5. Squares: low energy electron diffraction, Ref. 7 (110), Ref. 4 (100), Ref. 3 (111). Diamond: ion scattering spectroscopy, Ref. 6. Circles: medium energy ion scattering, Ref. 1.

energy. Since the atomic size of Pt is also larger than that of Ni it follows that Pt should segregate to the surface of Pt-Ni alloys independent of surface orientation. The segregation reversal is therefore not a trivial phenomenon and it appears that an explanation may only be obtained by a detailed analysis of the face dependence of the interatomic interactions.

From (1) it is seen that $V_\Lambda^{(1)} - V_{\text{bulk}}^{(1)}$ represents a linear contribution to the segregation energy and thus its sign and value directly control the segregation to a given layer. For example, a positive value of this term indicates that a negative σ_Λ would reduce the total energy of the system and hence c_Λ is expected to be less than 0.5. The $V_\Lambda^{(2)}$ interactions play a similar role, but being quadratic they typically

TABLE I. Calculated surface energies in J/m^2 for the low-index surfaces of pure Ni and Pt.

Element	(110)	(100)	(111)
Ni	2.68	2.55	2.56
Pt	2.43	2.45	2.28

TABLE II. Connolly-Williams interactions in degrees K for the low-index surfaces of $\text{Pt}_{50}\text{Ni}_{50}$ as functions of the layer number Λ .

Surface	Λ	$V_{\Lambda}^{(1)} - V_{\text{bulk}}^{(1)}$	$V_{\Lambda}^{(2)}$	$V_{\Lambda+}^{(2)}$	$V_{\Lambda++}^{(2)}$
(110)	1	539	679	3799	1401
	2	998	2160	3935	1201
	3	-111	2272	4005	
(100)	1	1131	1784	4460	
	2	-189	3810	4033	
	3	29	3756	4000	
(111)	1	1250	2607	4170	
	2	-761	4463	3328	
	3	0	4413	3325	

only influence the absolute value of the segregation and not its sign. Thus, if $V_{\Lambda}^{(2)}$ is positive, corresponding to an ordering behavior of the alloy, the enrichment of the Λ th layer by the segregated element will be weakened. The remaining terms $V_{\Lambda+}^{(2)}$ and $V_{\Lambda++}^{(2)}$ govern the composition in the Λ th layer relative to that of the two neighboring layers and positive values for these interactions will favor a concentration profile where the layers Λ and $\Lambda+1$ or Λ and $\Lambda+2$ are enriched by atoms of opposite kind.

Before we discuss the segregation profiles in terms of the calculated Connolly-Williams interactions it is important to note a number of facts. First, since the cluster function expansion (1) is an expansion over a complete basis set, its parameters are uniquely defined. Second, since our truncation is shown to be adequate and the expansion is found to be well converged, an analysis based on the interactions is physically meaningful. Third, since the interactions are obtained by first-principles calculations their signs and magnitudes are not directly amenable to a simple physical interpretation. However, the surface segregation profiles calculated by means of the extracted interatomic interactions may be given a physical interpretation in terms of the properties of the Connolly-Williams expansion.

In Table II we summarize the most important one- and two-site interactions obtained in the present work for the three low-index surfaces of a random $\text{Pt}_{50}\text{Ni}_{50}$ alloy. It is seen that $V_1^{(1)} - V_{\text{bulk}}^{(1)}$ is always positive and hence a Pt enrichment of the surface layer would be preferable for all three faces in the absence of any other interactions. This is completely in accordance with the fact that Pt has a smaller surface energy for all three faces and a larger atomic size. Considering now the subsurface layer we find that while $V_2^{(1)} - V_{\text{bulk}}^{(1)}$ for the (111) and (100) faces becomes negative, i.e., favors an enrichment by Ni in the subsurface layer, the sign of $V_2^{(1)} - V_{\text{bulk}}^{(1)}$ for the (110) face remains positive. In the latter case Pt would therefore segregate to the first as well as to the second layer if no other interactions were present. Hence, the subsurface layer of the (110) face, and this is a main difference compared to the (111) and (100) faces, behaves effectively as a surface layer in agreement with the facts that the interlayer spacing of a (110) face is only 60% of that of the (111) face and that the coordination number of a (110) subsurface atom is still one less than the bulk value. The small interlayer spacing is also reflected in the large

value of $V_2^{(1)} - V_{\text{bulk}}^{(1)}$ which is twice that of $V_1^{(1)} - V_{\text{bulk}}^{(1)}$. As will be shown below it is just this surface geometry related behavior of $V_2^{(1)} - V_{\text{bulk}}^{(1)}$ which is responsible for the segregation reversal at the (110) face.

We now turn to the two-site interactions listed in Table II. Here, the positive sign and large values of $V_{\Lambda}^{(2)}$ and $V_{\Lambda+}^{(2)}$ indicate a strong tendency towards ordering which is known to exist in the bulk Ni-Pt alloys and which is seen to be clearly surface index dependent. In particular, for the (110) and (100) surfaces $V_{\Lambda+}^{(2)}$ is larger than $V_{\Lambda}^{(2)}$ and for these surfaces the intralayer ordering tendency is less than the interlayer ordering and as a result we find for these surfaces a strongly oscillating concentration profile. In contrast to this, $V_{\Lambda}^{(2)}$ is greater than $V_{\Lambda+}^{(2)}$ for the (111) surface, except in the first layer, and therefore we only find a weak oscillation in the composition of the first three layers. This is in agreement with the fact that for an equiatomic alloy the composition of all (111) layers are equal, independent of whether the alloy is completely disordered or completely ordered in the $L1_0$ or $L1_2$ structures.

For the (110) surface we see that the interlayer two-site interactions $V_{1+}^{(2)}$ and $V_{2+}^{(2)}$ are much greater than the corresponding intralayer interactions $V_1^{(2)}$ and $V_2^{(2)}$ as well as the one-site interactions $V_1^{(1)}$ and $V_2^{(1)}$. Therefore, although the latter indicates a preference for Pt to segregate towards the surface and the subsurface layers, it turns out that the strong tendency to interlayer ordering leads to an oscillatory behavior of the surface concentration profile. For a two component alloy there are two possibilities with the opposite enrichment in the same layers, i.e., one with Ni on top and the other with Pt on top. This results in the existence of two minima (local and global) in the free energy within the multidimensional space of layer concentrations. The energy balance between them determines the type of surface segregation, and we found that the profile with Ni on the top is more stable. Basically, this is due to the fact that $V_2^{(1)} > V_1^{(1)}$, and therefore the preference for Pt to enrich the subsurface layer is stronger than it is for the surface layer. The preference for Ni to enrich the third layer is indicated by the negative value of $V_3^{(1)}$ which also makes the segregation profile with Ni on top more stable.

To check this result we have calculated by the LMTO-CPA method the surface energies of the (110) surface with three monolayers on the top of the $\text{Pt}_{50}\text{Ni}_{50}$ alloy in the sequences Ni/Pt/Ni and Pt/Ni/Pt corresponding to the different types of the segregation profiles. In both cases the surface energies obtained, 2.49 J/m² for the Ni/Pt/Ni sequence and 2.66 J/m² for the Pt/Ni/Pt sequence, were smaller than that of the uniformly random alloy surface, 2.77 J/m². Thus, one would expect a strongly oscillating surface profile. In complete agreement with our mean-field results, the direct total energy calculation also showed that the profile with Ni on top is more stable than that with Pt on top. Hence, the strong oscillations of the surface profile and the segregation reversal are driven by the energetics and not by the entropy.

Lundberg⁸ also reported the existence of two minima in the free energy for the oscillatory profiles with different types of atoms on top. In his EAM calculations the energy balance was easily disturbed by a variation of the interlayer

distance at the surface, and as a result he concluded that surface relaxation effects accounted for the existence of the segregation reversal. According to the present results such an influence of surface relaxation on the energy balance is to be expected, i.e., as the interlayer distance between the surface and subsurface layer is decreased, the subsurface atoms come even closer to the surface which in turn will increase the value of $V_2^{(1)}$. However, the relaxation effects themselves are not responsible for the segregation reversal in the Pt-Ni alloys. Rather, its origin is the strong ordering tendency of the system and the open geometry of the (110) surface.

The discussion of the oscillatory surface profiles and the segregation inversion in $\text{Pt}_{50}\text{Ni}_{50}$ may be summarized in the following simple picture. The segregation profiles in the Ni-Pt system are governed by two main trends: (a) the tendency for Pt to enrich the surface on account of the fact that it has a smaller surface energy and a larger atomic size than Ni and (b) the tendency to intralayer and interlayer ordering which results in a more [(100) and (110) faces] or less [(111) face] pronounced structure of alternating Pt and Ni layers.

For the closely packed (111) and (100) surfaces this leads in a natural way to oscillatory segregation profiles with Pt on top. In the case of the more open (110) face, where the interlayer distance is small and where the coordination numbers of the subsurface atoms do not reach the bulk values, Pt atoms trend to segregate not only to the surface but also to the subsurface layer. This is of course in conflict with the tendency to form a structure of alternating layers and since the tendency for Pt atoms to enrich the subsurface layer is found to be stronger than the tendency to enrich the surface layer the frustration results in the observed segregation inversion.

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